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COMMUNICATION

The effect of peripheral bipyridine ligands on the photocatalytic hydrogen production activity of Ru/Pd catalysts†

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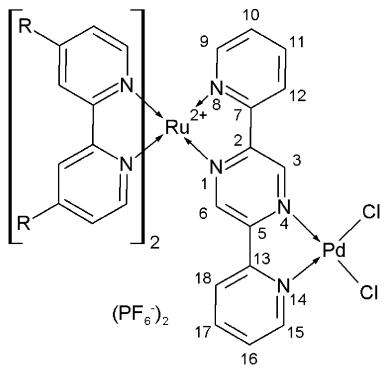
A pyrazine bridged ruthenium/palladium bimetallic photocatalyst with peripheral 4,4′-dicarboxyethyl-2,2′-bipyridine ligands, EtOOC-RuPd, is reported, together with its 2,2′-bipyridine analogue. Upon irradiation with visible light, EtOOC-RuPd catalyses the production of hydrogen gas whereas the complex RuPd does not.

Hydrogen is widely perceived to be one of the primary replacement fuels, in particular for transport, due to its exceptionally high energy density/mass ratio. The photocatalytic production of hydrogen is therefore a major challenge in converting solar energy directly to chemical energy. One of the most promising approaches towards this goal is the use of molecular photocatalysts that utilise visible light to drive proton reduction and it can be envisaged that such systems comprise of a light-harvesting antenna (photosensitiser) that can donate electrons to a catalytically active centre to which it is connected *via* a bridging ligand.

Due to their exceptional photophysical and redox properties Ru(II) polypyridyl complexes are an excellent choice as the light harvesting centre while Pd(II) or Pt(II) are the metal of choice for the catalytically active centres.[1] Alternative combinations already reported are Re/Co, Ru/Pd, Ru/Pt, Os/Rh, Ru/Rh, Pt/Co, Ir/Rh.[2–10] The intramolecular approach in which a bridging ligand facilitates photoinduced electron transfer from the light harvesting centre to the hydrogen forming centre requires vectorial electron transfer to be mediated by the bridging ligand. This realisation has led to the application of bridging ligands that are more electron deficient than the peripheral ligands. However, recently Rau *et al.* have proposed that in addition to the final (lowest lying) excited state, higher lying excited (Franck–Condon) states can also play an important role, as seen from the excitation wavelength dependency of turnover numbers (TONs).[11] However, other factors such as lifetime of the charge separated states and secondary processes during the multiple electron transfer steps may influence catalytic activity.

Here we report direct evidence of the importance of the peripheral 2,2′-bipyridyl (bpy) ligands in the photocatalytic process. The photocatalytic activity of the Ru(II)/Pd(II) complex based on the non-substituted 2,2′-bipyridyl (bpy) ligand (**RuPd**) is contrasted with that of the analogous heterobimetallic complex in which the more electron deficient 4,4′-di(carboxyethyl)bipyridine ligand replaces bipy (*i.e.* **EtOOC-RuPd**). The structures of both complexes are shown in Fig. 1. The bridging ligand is 2,5-di(pyridin-2-yl)pyrazine (2,5-dpp).



R = H (**RuPd**), COOEt (**EtOOC-RuPd**)

Fig. 1 Structure of complexes described in the text.

In agreement with the earlier report by Sakai and Ozawa,[12] the complex **RuPd** was found to show no photocatalytic activity towards hydrogen production. In stark contrast we found that the dinuclear catalyst **EtOOC-RuPd** could achieve TONs for H_2 production of up to 400 (32 μmol after 18 h).

Photocatalytic reactions were performed by irradiation of the reaction mixtures at 470 nm using triethylamine (TEA) as the terminal reductant to regenerate the Ru(II) complex. The presence of water was found to be a key factor for photocatalytic hydrogen production,‡ with hydrogen formation not observed in its absence. The role played by water in the catalysis is however manifold: (1) as a source of protons, and hence an increase in water content accelerates to a certain point the reaction, (2) to facilitate

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† Electronic supplementary information (ESI) available: Synthesis of **Ru**, **RuPd**, **EtOOC-Ru** and **EtOOC-RuPd** and experimental details on the catalysis. See DOI: 10.1039/c1dt11241d

proton-transfer and (3) to increase solvent polarity thereby stabilizing polar intermediates. Control experiments with the mononuclear precursor compounds **Ru** and **EtOOC-Ru** confirmed the necessity of the presence of the Pd(II) centre. The time-dependence of dihydrogen formation is shown in Fig. S2 (ESI†). Different behaviour is observed for the preformed complex **EtOOC-RuPd** and the *in situ* formed complex (*i.e.* **EtOOC-Ru** + $Pd(CH_3CN)_2Cl_2$, 1 : 1 molar ratio). Both graphs show a sigmoidal time profile eventually reaching a plateau that indicates deactivation of the catalyst. An induction period was observed with dihydrogen production reaching a maximum after *ca.* 3.5 h for **EtOOC-RuPd** and *ca.* 5.5 h for **EtOOC-Ru** + $Pd(CH_3CN)_2Cl_2$. The longer induction period for the *in situ* formed binuclear complex supports the conclusion that the active catalyst is a binuclear **EtOOC-Ru/Pd** complex. For further details on the photocatalytic reactions see the ESI.†

Colloid formation has been discussed as a possible process in catalysis with Ru/Pd complexes[13,14] and although this behaviour cannot be excluded in the present system it is important to note that the formation of a precipitate was not observed during the photocatalysis with either **RuPd** or **EtOOC-RuPd**.§

Previous investigations have shown that the 2,5-dpp bridge enables relatively strong coupling between the metal centres and that the emissive state for the $[(bpy)_2Ru\text{-}(2,5\text{-}dpp)]^{2+}$ and $[(bpy)_2Ru\text{-}(2,5\text{-}dpp)\text{-}Ru(bpy)_2]^{4+}$ compounds is dpp-based.[15–23] Absorption spectroscopy shows that **RuPd** and **EtOOC-RuPd** have similar features with the intraligand and metal-to-bpy charge transfer bands being shifted towards lower energy by *ca.* 15–40 nm. However, the lowest energy MLCT of **EtOOC-RuPd** is shifted by 10 nm to higher energy compared with the **RuPd** complex (Table 1). Similarly the emission spectrum of **EtOOC-RuPd** is shifted by 30 nm to the blue compared to **RuPd**. Due to the lower π* energy of the EtOOC-bpy ligands they are better π-acceptors which leads to a stabilisation of the ground state and is manifested in a red shift of 40 nm in the ^{1}MLCT ← GS transition involving the peripheral bpy/$(EtOOC)_2$bpy ligands. This is in agreement with the higher oxidation potential of **EtOOC-RuPd** with respect to **RuPd**. These data suggest as expected that the π*-energy levels for the carboxyethyl ligands are lower in energy than those of the bpy ligands. The UV/Vis absorption spectrum of the complex undergoes several changes already when TEA is added, as indicated by absorption and emission spectroscopy. Similar changes are observed when following the photocatalysis by absorption spectroscopy, assigned tentatively to exchange of the chloride ligands.

Table 1 Photophysical and electrochemical properties of the dinuclear complexes **RuPd**, **EtOOC-RuPd** and their mononuclear precursors **Ru**, **EtOOC-Ru**

Compounds	Abs. (log ε)/nm	Em./nm	τ^a/ns	Oxidation^b/mV
RuPd	539 (4.00)	807	< 0.5	+1.56
EtOOC-RuPd	526 (4.20)	778	< 0.5	+1.75
Ru	483 (3.98)	685	266	+1.33
EtOOC-Ru	467 (4.25)	630	564	+1.68

[a] Determined by time correlated single photon counting at 293 K in aerated acetonitrile solution. [b] From cyclic voltammetry in acetonitrile (0.1 M $TBAPF_6$) *vs.* Ag/AgCl. All data were acquired at 293 K.

The dramatic differences in the photocatalytic activities towards H_2 production between the polypyridyl-Ru/Pd complexes **RuPd** and **EtOOC-RuPd**, *i.e.* with the former inactive and the latter highly active (TONs of 400), is surprising. Both heterobimetallic complexes exhibit very short excited state lifetimes, indicating efficient interaction between the two metal centres (electron transfer quenching). The observations indicate the importance of the peripheral ligand for photoinduced electron transfer as proposed earlier by Rau *et al.*[11] It is also important to note that hydrogen formation is not directly linked to the formation of precipitates as is observed for other systems.[14]

Further investigations concerning the nature of the electron transfer and additional factors governing the overall catalytic activity of intramolecular photocatalysts such as the nature and location of the involved electronic states are in progress.

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Notes and references

‡ TONs were determined by gas chromatography after irradiation of the reaction mixture for 18 h. Reaction mixture: c(cat.) = 4.08×10^{-5} M, c(TEA) = 2.15 M, 5 vol% of water in acetonitrile. The mixture was irradiated with an LED torch at 470 nm. The TON is the average of three independent measurements.

§ The addition of mercury has been proposed as a method to identify the involvement of colloids (by quenching their activity). In the present system however addition of mercury leads to decomposition of the complexes even in the absence of light and hence this standard test is not applicable here. It should be noted that the coordination of $PdCl_2$ to both **Ru** and **EtCOO-Ru** would be essentially the same and hence dissociation to form Pd-colloids would be expected from both complexes if it occurred. The absence of H_2 evolution in the case of **RuPd** suggests that Pd dissociation to yield an active colloid does not occur in the present system.

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